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Angle-Dependent Optics of Plasmonic Core-Shell Nanoparticles

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14. ABSTRACT The objective of this proposal was to study angle-dependent scattering from individual plasmonic core-shell nanoparticles placed on a dielectric substrate. The PI synthesized gold and silver metallic core metallic shell nanoparticles. After creation of the core shell nanoparticles, the PI used an optical microscopy technique called Fourier plane optically microscopy to image the far field angular optical response from individual nanoparticles. The technique and results were passed to collaborators at AFRL/RW.					
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Angle-Dependent Optics of Plasmonic Core-Shell Nanoparticles

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Objective

The objective of this proposal was to study angle-dependent scattering from individual plasmonic core-shell nanoparticles placed on a dielectric substrate. The core-shell architecture that we planned to study will be of bimetallic core-shell nanoparticle variety. We will utilize Fourier-plane optical microscopy method to resolve the angular scattering as a function of spherical co-ordinates: azimuthal and polar angles.

Absorption, scattering and emission of light from nanoparticles, especially when they are placed on a substrate, can drastically depend on angle of excitation and angle of scattering/emission. Such particle-substrate coupling can influence the gain of an optical antenna, which is essentially a product of field enhancement and directivity. Core-shell nanoparticles are single nano-scale entities with inherent inhomogeneity. This inhomogeneity can further influence its interaction with light.

Until now, most of the plasmonic core-shell nanostructures have been studied in aggregates and assemblies. This leads to averaging of optical properties. In order to unveil the fundamental optical interaction of plasmonic core-shell nanoparticles with light, it is imperative to study them in isolation, and herein we performed some experiments on nanoparticle arrays.

Approach

The core-shell nanoparticle that we used was chemically prepared using well established synthesis protocols. We will concentrate our efforts on studying metallic core metallic shell. The metals that we used were mainly gold and silver, as their plasmonic response in visible

and infrared region is strong, and can be accurately tuned by varying the size of the core and shell sizes.

To study the angle dependent scattering, in the coming months, we will be using an emerging optical microscopy technique called as Fourier-plane optical microscope to directly image the far-field angular optical response from individual plasmonic core-shell nanoparticles. This method will provide intensity distribution of scattering/emitted light as a function of spherical co-ordinate angles (polar and azimuthal). From these angular intensity distributions, we will be able to unveil order and nature of plasmon resonance (dipolar, quadrupolar, etc.) at single nanoparticle level. Importantly, these measurements will be performed in the visible and near infrared regime, thus addressing a large bandwidth of frequencies relevant to optical antennas at nanoscale. All the performed measurements will be corroborated with numerical simulations based on finite difference time domain (FDTD) method and finite element method (FEM). Specifically, we will simulate the effect of size and mechanical distortion in core-shell nanoparticles on its angle-dependent plasmon resonant scattering.

Collaboration:

- The work, especially on the numerical simulation, is been carried out in collaboration with AFRL scientists: Monica Allen and Jeffery Allen.

Preliminary results:

Figure 1 shows the formation of periodic arrangement of core-shell NP assemblies on Si wafer. Here electron beam lithography has been used to generate the periodic binding spots for the NPs. Proper chemical functionalization of the binding spots and Au NPs enable Au NPs to adhere, thus forming hot NP junctions in a periodic fashion. Strong electrostatic interaction between the negatively-charged Au NP surrounded by ionic double layer and the positively-charged amino groups has been utilized to immobilize Au NPs onto silanized glass and silicon wafer surface. Cover slips or silicon wafer was first treated with piranha solution to make the surface hydrophilic. The hydrophilic surface will facilitate the functionalization process required to adhere the Au NPs. Both silicon wafer and glass slides have silanol (Si-OH) groups on their surface which react readily with APTES to construct the $-NH_2$ group yielding a monolayer of APTES on the surface of the substrate. Washing the substrate with

water removes excess APTES. The substrate was annealed at 120 °C. The APTES modified substrates were immersed into an aqueous solution of citrate-stabilized Au NPs for 6 hours, thoroughly washed with water, and subsequently dried with N₂ gas. Two approaches were taken for the APTES modification of the substrate. In one attempt, hydrophilic substrate was first chemically functionalized using 2% aqueous solution of APTES to form monolayer of APTES and in the next step EBL was performed on that substrate. In the other attempt, first EBL was performed on the substrate to form trenches and then it was treated with aqueous solution of APTES. As PMMA is inert towards silanization due to the unavailability of surface –OH groups, only monolayer by APTES should form in the trenches because of exposed silanol groups. For the former case, repeatedly it was found that NPs are sitting in the trenches in an irregular pattern which indicates that somehow the homogeneity of APTMS monolayer is lost after EBL is done. The second approach of functionalizing the trench after EBL yielded regular array of NPs. Particularly ‘V’ shaped trench formation was undertaken keeping in view the asymmetric behavior towards wavefront for a V shaped nanoantenna. It should be noted that the coating speed and concentration of PMMA was adjusted such that the thickness of PMMA layer was around 120 nm. If the thickness of the PMMA layer is too high, functionalization of trench and consequently adhesion of Au NPs become less facile. As the Au NP dimension was around 60 nm, the width of the trench was kept at 75 nm to ensure single NP accommodation along the two axes of the ‘V’ shaped trench. After dipping the substrate overnight in the citrate functionalized Au NPs, it was observed that only few NPs were sitting in the trench in a random fashion. So, it was necessary to change the width of the trench. Two other trenches with different width viz. 100 nm and 120 nm were fabricated and most regularized array of Au NPs was obtained using the former trench (Figure 2). In all these cases outside length of both axes of ‘V’ trench was set at 600 nm and the angle between two axes as 80 °. Optimization of the trench dimension and the concentration of Au NP were done simultaneously. Optimum concentration of Au solution was found to be 1/5th of the concentration of as prepared Au NP solution. More concentrated Au NP solution yielded unnecessary random patches of Au NP aggregates throughout the surface of the substrate. After the formation of Au NP array, the substrate was cleaned with N-methyl pyrrolidone, which will take off only the PMMA, leaving the periodic pattern of ‘V’ shaped NP array on bare substrate. Formation of this periodic pattern can be clearly evidenced from the FESEM image (Figure 2a). Au NPs were immobilized also in a big ‘B’ shaped trench made by EBL at the corner of the pattern which helps to correlate the electron and optical microscopic image. Distance from one ‘V’ shaped NP array to other was

maintained as 10 μm in both sides. One representative magnified image of such array constituting the periodic pattern has been shown in Figure 2b. From Figure 2b, it can be clearly seen that the Au NPs are forming a monolayer along the two axes of 'V' antenna. SERS investigation was carried on one 'V' antenna. Successful immobilization of Au NPs in other two periodic patterns of 'V' antennas having intermediate distances of 10 μm and 2 μm along the axes and the other having 2 μm along both axes shows the reliability of the procedure.

Here, we describe the polarized SERS response of single 'V' antenna with the Raman marker molecule Nile blue chloride. Typical SERS spectra of Nile blue from a 'V' antenna under different polarizations (0° to 90° polarization angle) has been shown in Figure 3a. Change of polarization on the 'V' antenna has been depicted pictorially by the inset diagram of Figure 2b. Intensities of the peak at 587 cm^{-1} were noted for different polarizations and they were plotted against their corresponding polarization angles. Maximum intensity was obtained at 45° polarization angle, as evident from Figure 3b.

Figures

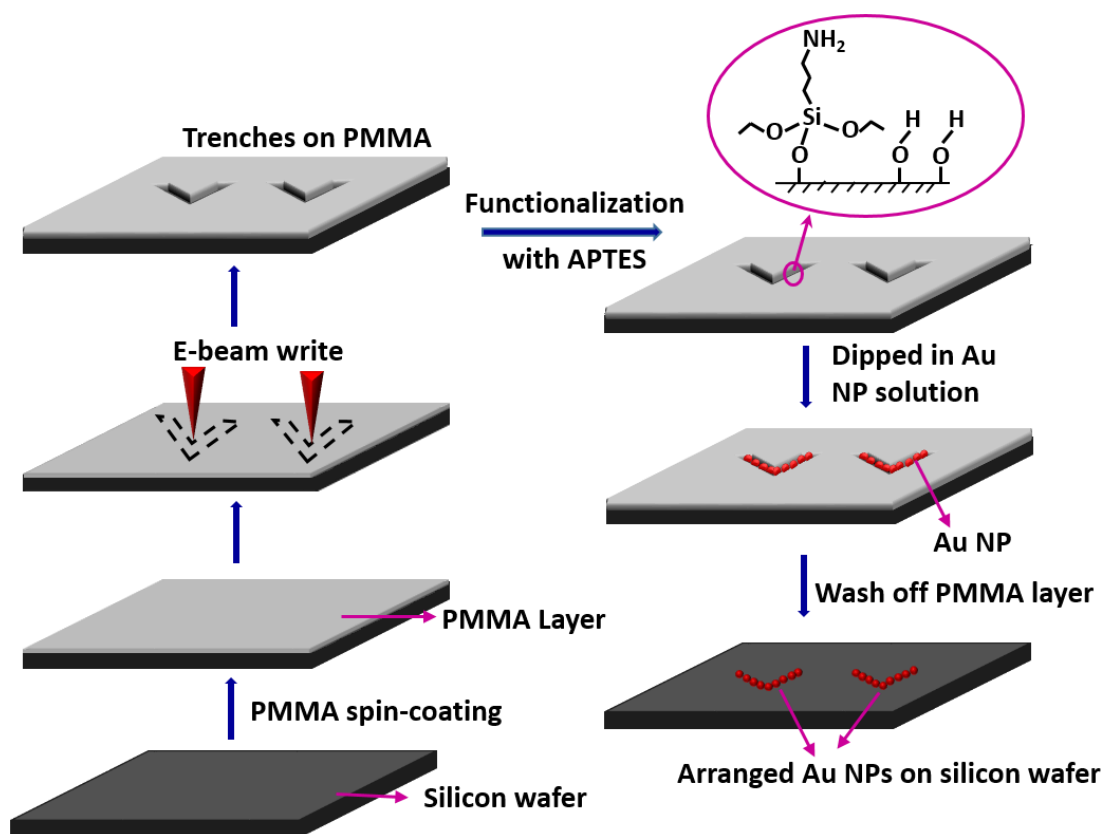


Figure 1. Step by step schematic illustration showing the formation of periodic pattern of 'V' antennas constituting Au NPs on silicon wafer.

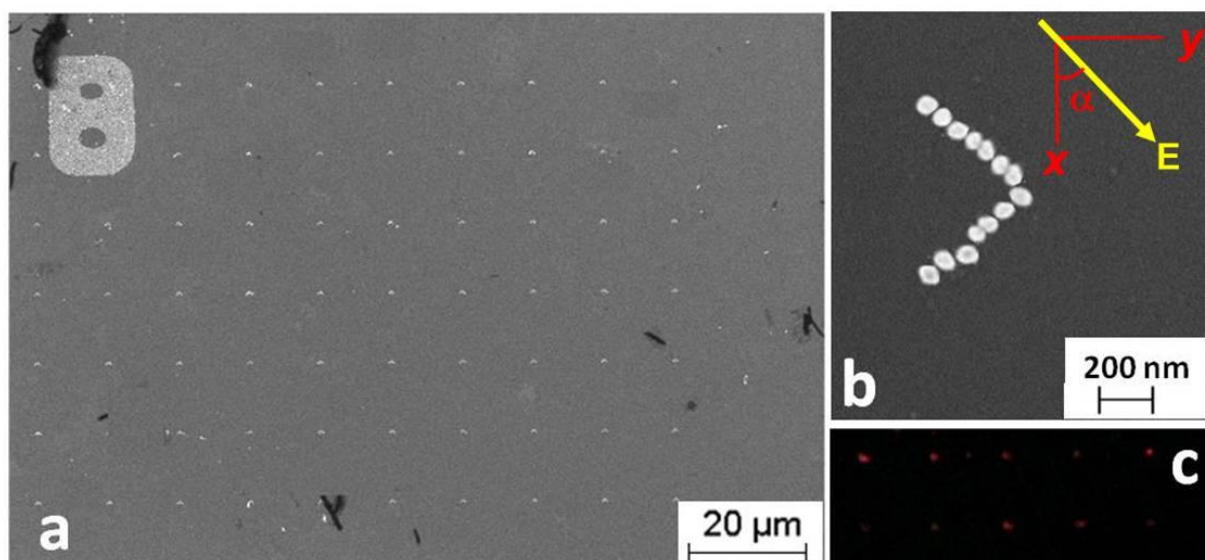


Figure 2. (a) FESEM image of a 100 x 60 μm periodic arrangement of 'V' shaped Au NP arrays, letter B has been written in the corner for the ease of correlation study, (b) One such 'V' antenna in high magnification showing the monolayer arrangement of Au NPs. Single 'V' antenna is illuminated using a focused LASER of 633nm illumination wavelength. Top right corner shows the direction of incident light where α is the polarization angle, (c) Dark field image of two rows of periodic arrangement, showing the reddish bright dots as the 'V' antennas.

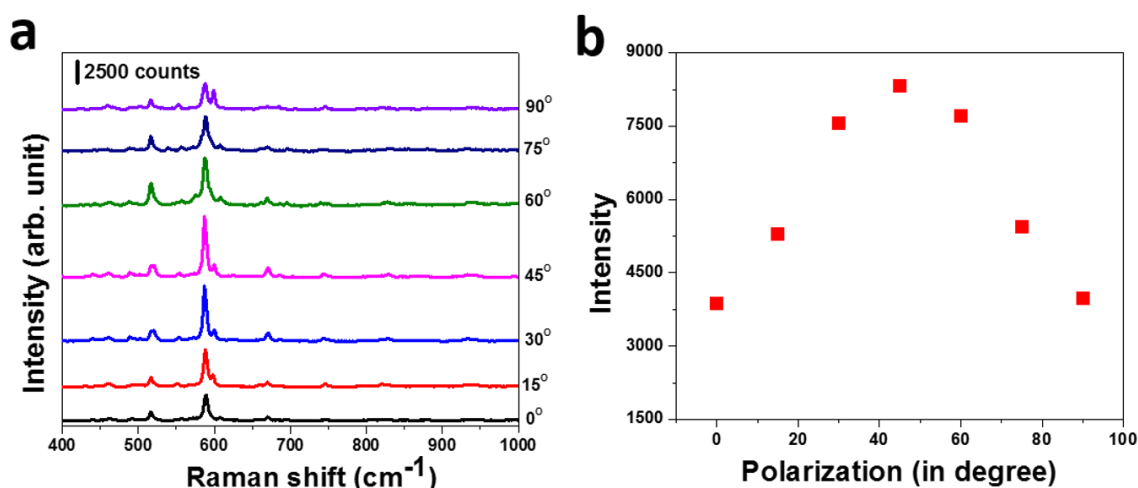


Figure 3. (a) Polarization dependent SERS spectra of a 'V' antenna and (b) the corresponding intensity vs polarization angle plot.